Polymer Bulletin 27, 585–589 (1992)

Polymer Bulletin

On the abnormal exponents a_η and a_D in Mark Houwink type equations for wormlike chain polysaccharides

M. Rinaudo

Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS),
B.P. 53 X, F-38041 Grenoble Cedex, France

Summary

The Mark Houwink exponent relating intrinsic viscosity and the molecular weight are usually much larger for polysaccharides than for synthetic polymers. In a moderate range of molecular weights, it depends directly on the stiffness of the molecules considered as worm like chains. This paper demonstrates that these exponents are predictible from the model of Yamakawa -Fujii.

Introduction

It is established that for cellulose derivatives (1) or polysaccharides such as scleroglucan (2) succinoglycan (3) and xanthan (4), the a_η exponent in the Mark Houwink relation between intrinsic viscosity $[\eta]$ and molecular weight is higher than for usual synthetic polymers ; in this last case, the theory for hydrodynamic properties of non-draining random coil more or less expanded by the excluded volume effect is $0.5 \leq a_\eta \leq 0.8$ (5).

In that case also, it comes :

$$3a_D + a_\eta = -1.$$

with a_D the exponent relating the diffusion coefficient to the molecular weight.

For a wormlike chain, Yamakawa-Fujii established the relation between hydrodynamic parameters and molecular weight taking into account the deviations from the randon coil statistics and the non-draining behaviour (6,7). In this treatment, the excluded volume effect is not considered then it treholds for theta conditions only.

Recently, Bohdanechy et al (5) discussed the relation between these exponents and the reduced contour chain length L_r of the molecules.

In this treatment, L_r is taken as $L_r = L/\lambda^{-1}$ with λ^{-1} the Kuhn segment which equals 2Lp, i.e 2 times the persistence length and L the contour length of the molecule. From this work, $(a_\eta)_\theta$ and $(a_S)_\theta$ (with $a_S = 1 + a_D$) were demonstrated clearly not to be equal to 0.5 for wormlike chain even in θ-conditions ; they should go to 0.5 for the limiting values $L_{r \rightarrow \infty}$.

As expressed by Bohdanechy, as $L_r \leq 100$, a_x varies as a consequence of the non-gaussian character of chains and of weak hydrodynamic interaction. In addition, in the range of lower L_r values, the excluded volume effect may remain small (8).

Recently, Fujita examined the unsolved problems on dilute polymers solutions (9) ; he discussed the onset for excluded volume effect for semi flexible chains and introduced a critical value over which it has to be considered ($Lc \simeq 100$ Lp or $Lr \simeq 50$).

This paper concerns the discussion on few experimental data obtained on polysaccharides.

Results and discussion

From previous experimental data on xanthan gum (10, 11) alginic acid (12) and hyaluronic acid (13, 14) the intrinsic persistence lengths Lp were determined for infinite ionic strength ; the values were in the range 350-450A° for xanthan, 80-100 A° for alginic acid and hyaluronic acid ; these values may be assumed to correpond to θ conditions values.

Furthermore on a flexible polyelectrolyte (Na-polystyrene sulfonate), the values of [η] extrapolated to infinite ionic strength in NaCl agree with unperturbed values and give a Mark Houwink exponent $a_\eta \simeq 0.5$ (15). This conclusion allows us to point out that the electrostatic excluded volume, the main excluded volume contribution, is screened for infinite ionic strength (in 1M NaCl solution, the Debye length equals 3A° ; in our conditions, it becomes negligible).

From the values of L_p, using Yamakawa-Fujii treatment (6, 7), L_r, a_η and a_D were determined allowing us to plot a_η and a_D as a function of the molecular weight of the considered polymers (Figures 1 and 2) (8). The curves should correspond to infinite ionic strenght conditions i.e. in absence of electrostatic excluded effect. The experimental values are then compared with the prediction.

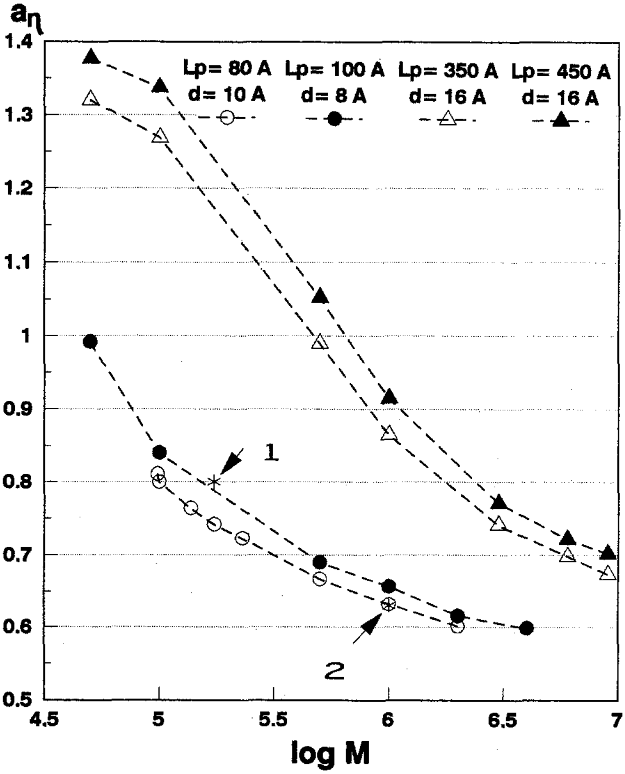

FIGURE 1 : Viscometric exponent a_η predicted from Yamakawa-Fujii model for xanthan (▲ , Δ) and alginic or hyaluronic acid (● , ○). Comparison with experimental values. → (1) Alginate (12) ; (2) Hyaluronic acid (14).

For xanthan, in the range of $3\times10^5<M<9\times10^6$, the experimental value is $a_\eta = 1$; this value is still larger than predicted by this treatment (0.8-0.9). In fact, it seems that aggregates may disturb the viscosity-molecular weight dependence ; xanthan is perhaps a bad test for this discussion.

In the range of molecular weights tested, for alginic acid (rich in guluronic acid), the agreement is good ($a_\eta = 0.8$) (12) as well as for hyaluronic acid (14) ($a_\eta = 0.63$) using the set of parameters $L_p = 80$ A° and a diameter 10 A° (16). Usually, the polymers are investigated in a reduced range of molecular weights and a_η is determined as the slope of the best linear fit of the dependence log $[\eta]$ (log M).

From Yamakawa-Fujii (7), the intrinsic viscosity $[\eta]_\theta$ can be estimated from the relation :

$$[\eta]_\theta = \phi\ (L_r, d_r)\ (M_L\ \lambda)^{-3/2}\ M^{1/2}$$

with L_r and d_r the reduced contour length and diameter ; M_L the mass per unit length and $\lambda^{-1} = 2L_p$; L_r equals the number of Kuhn segments in the semi-rigid chain. The calculated values are compared with experimental values extrapolated for infinite ionic strength for some polymers in Table 1. The agreement looks better in the range of lower molecular weights, specially with alginates.

Assuming the validity of this treatment, the a_η in presence of electrostatic excluded volume effect i.e. at a given ionic strength can be predicted as a first approximation by the relation :

$$a_\eta \simeq a_{\eta\infty} + 3\ \varepsilon$$

in wich ε is determined from the relation $\alpha_\eta \sim M^{\varepsilon}$ in which the viscometric expansion factor α_η is calculated as usually (10).

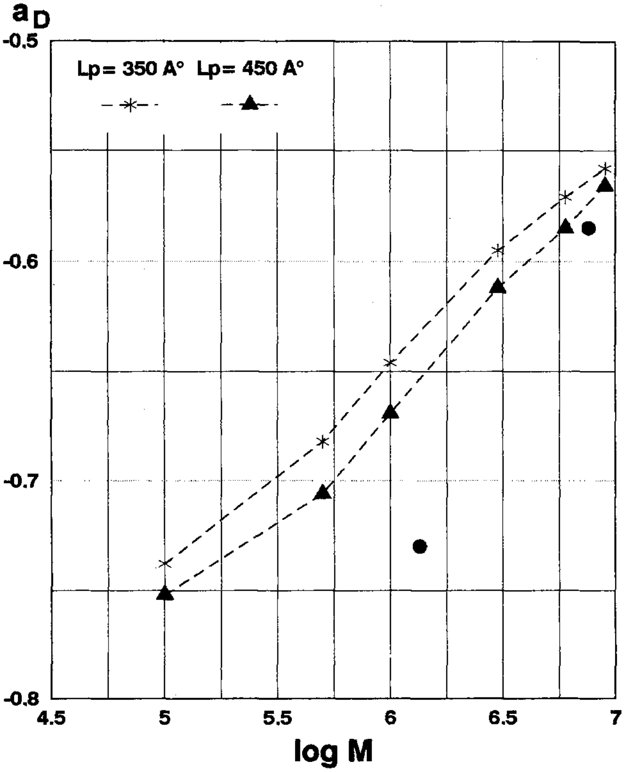

FIGURE 2 : Translational diffusion exponent a_D predicted for Xanthan (✱;▲). Comparison with experimental values (●).

The exponants a_D were also estimated from Yamakawa-Fujii for xanthan. The experimental self diffusion coefficient were determined in the dilute regime by fringe pattern (fluorescence) bleaching technique (11) on a series of xanthan. The following dependence was given by Tinland (17) :

$$D \sim M^{-0.56}$$

The experimental values of a_D determined for pair of samples in NaCl 0.1N are shown in Figure 2. These data are in relatively good agreement with the prediction, assuming that the electrostatic repulsion is screened even if the values were not obtained for infinite ionic strength.

Conclusion

The aim of this paper was to justify the abnormal exponents a_η and a_D usually found on many polysaccharides. Based on a worm like chain model and the treatment of Yamakawa-Fujii, it is demonstrated that in θ-conditions in the range of molecular weights available ($10^5 < \overline{M}w < 10^7$) the asymptotic regime is never attained.

These polymers never behave as random coil but as non gaussian chains (L_r < 100) with weak hydrodynamic interaction.

This was also demonstrated from the low values obtained experimentally for the ratio R_h/R_G (R_h = hydrodynamic radius from translational diffusion and R_G = radius of gyration) (11).

The experimental values obtained for polyelectrolytes (xanthan, alginate, hyaluronate) for infinite ionic strength (or 10^{-1}N) seems to be valid and in good agreement with theoretical predictions. From this discussion, its is predicted that a_η (and also a_D) deviates more from $|0.5|$ in unperturbed conditions when the stiffness of the polysaccharides increases (i.e. L_p increases, see figure 1). This conclusion is only adapted for θ conditions and demonstrates that these semi-rigid polysaccharides have never to be considered as coiled polymers.

Tableau 1. Comparison between experimental and calculated values of $[\eta]\theta$

a) for xanthan

Mw	$[\eta]\theta$ ml/g (17) exp	*$[\eta]\theta$ ml/g calc
8.7×10^6	7149	9700
2.8×10^6	2173	4356
8×10^5	625	1890
6.4×10^5	479	1360

* L_p = 310 A° ; d = 16 A° ; M_L = 92g/A°

b) for Na-alginate

Mw	$[\eta]\theta$ ml/g exp (12b)	*$[\eta]\theta$ ml/g calc
2.3×10^5	740	622
1.73×10^5	525	499
1.37×10^5	460	415
9.85×10^4	350	318

*L_p = 80 A° ; d = 10 A° ; M_L = 40g/A°

References

1. Bandrup, J.; Immergut, E.H. (1975) in "Polymer Handbook" 2d Edition Wiley IV-31-33
2. Norisuye, T.; Yanaki, T.; Fujita H. (1980) J. Polym. Phys. Ed. 18:547
3. Gravanis, G.; Milas, M.; Rinaudo, M.; Tinland, B. (1987) Carbohydr. Res. 160:259
4. Rinaudo, M.; Milas, M. (1987) in: Yalpani, M. (ed) "Industrial Polysaccharides, Genetic engineering, Structure/property relations and application" Elsevier Publ. pp. 217-223
5. Reddy, G.V.; Petrus, V.; Bohdanecky, M. (1990) Makromol. Chem. Rapid Commun. 11:355
6. Yamakawa, H.; Fujii, M. (1973) Macromolecules 6:407
7. Yamakawa, H.; Fujii, M. (1974) Macromolecules 7:128
8. Bohdanecky, M. (private communication)
9. Fujita, H. (1988) Macromolecules 21:179
10. Tinland, B. ; Rinaudo, M. (1989) Macromolecules 22:1863
11. Tinland, B.; Maret, G.; Rinaudo, M. (1990) Macromolecules 23:596
12. a) Rinaudo, M. ; Graebling, D. (1986) Polymer Bull 15:253
    b) Bouffar-Roupe, C. (1989) Thesis (Grenoble, France)
13. Ghosh, S.; Li, X.; Reed, C.E.; Reed, W.F. (1990) Biopolymers 30:1101
14. Fouissac, E. (1991) Thesis (Grenoble, France)
15. Desbrières, J. (1980) Thesis (Grenoble, France)
16. Cleland, R.L. (1984) Biopolymers 23:647
17. Tinland, B. (1989) Thesis (Grenoble, France)

Accepted October 30, 1991 C